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THE OXIDATION OF HYDROQUINOL IN THE PRESENCE OF ALIPHATIC AMINES

BY ROLLA N. HARGER¹

DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY

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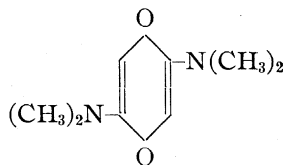
That hydroquinol is converted by oxidation in neutral and acid solutions into quinone, with the intermediate formation of quinhydrone, was first demonstrated by Wöhler in 1844.² This reaction appears to proceed quantitatively and the change can be brought about by the use of a great variety of oxidizing agents.

When we turn, however, to the oxidation of hydroquinol in alkaline solution the situation is far more complicated and at present we must admit that we have not an accurate understanding of the various changes which take place. The writer's interest in this phase of the subject resulted from the observation that an aqueous solution of hydroquinol, made strongly alkaline with methylamine, rapidly absorbs oxygen gas at ordinary temperatures with formation of a brilliant purple colored compound which is characterized by its pronounced crystalline habit.

It is of course well known that alkaline solutions of hydroquinol absorb oxygen, but if one will substitute an aliphatic amine, like methylamine, for the alkali usually employed he will observe an absorption of oxygen which is unusual both for its rapidity and in regard to the quantity consumed. The characteristic reactions which take place under these conditions appear to have not been studied.

For example, if hydroquinol is dissolved in a strong aqueous solution of mono- or dimethylamine and this solution is placed in a tube and exposed to oxygen, the liquid rapidly assumes a brownish red color and within an hour the deposition of a considerable quantity of beautiful red plates is observed. At the end of twenty-four hours the solution is almost filled with these brilliant crystals and for each gram of hydroquinol used there is absorbed about 250 cc. of oxygen. If the oxidation is continued for two or three days more the total absorption will increase to 500–600 cc. of oxygen per gram of hydroquinol, or from 10 to 12 equivalents of oxygen for

each molecule of hydroquinol. The colored crystalline compounds formed under such conditions are very stable and can be easily purified. The compound formed by the oxidation of hydroquinol in the presence of dimethylamine melts at 171° and is to be expressed by the formula $C_{10}H_{14}O_2N_2$. While its constitution has not yet been completely established it appears to be identical with tetramethyl diamino-quinone which was obtained by Mylius³ by treatment of benzo-quinone with dimethylamine, and to which Kehrmann⁴ has assigned the structural formula:



Aliphatic derivatives of this type are analogous in constitution to di-anilino-quinone which Hofmann⁵ prepared by interaction of aniline with quinone. While a large number of these anilino-quinones have been synthesized, an examination of the literature has shown that only four other representatives of these aliphatic amino quinones are known: the methyl-amino derivatives of toluquinone,⁶ 2-5 xyloquinone,⁷ and thymoquinone,⁸ and the ethylamino derivative of thymoquinone.⁶ These were prepared by interaction of the amine and quinone with yields which were said to be very low. The above mentioned oxidation of hydroquinol appears, therefore, of special interest as a simple, efficient means of preparing these aliphatic amino quinones, which latter compounds seem to present a chemical field as yet very little developed.

A somewhat analogous oxidation in the naphthalene series has been recorded by Plimpton.⁹ He prepared amino derivatives of naphthoquinone by the action of amines upon naphthoquinone and notes that these compounds are also produced when a solution of naphthoquinol and the amine is exposed to the air. The resulting product, however, was a *mono*-aminoquinone and not a *di*-aminoquinone such as we appear to have with the benzene series.

The brilliant purple compounds corresponding to formula I are not the only products resulting from this oxidation of hydroquinol and aliphatic amines. The yield of these purple compounds never approaches quantitative values, and on concentrating the filtrate to expel the excess of free amine there is deposited, upon cooling, a considerable amount of dark yellow crystals indicating at least another compound. This latter is now being investigated. It has also been found that when an aliphatic amine is added to hydroquinol the first product of reaction is a double compound or addition product of the amine and hydroquinol. Several such com-

binations have already been prepared and isolated. Whether they form an intermediate step in the process of oxidation cannot be stated at present with certainty. It has also been observed that the oxidation proceeds rapidly even in air, and quite as well in alcohol as in water.

Research is now in progress dealing with the oxidation of hydroquinol, and its homologues toluquinol, xyloquinol, etc., in the presence of various aliphatic amines. The detailed results of this work will be published later in the *Journal of the American Chemical Society*.

¹ NATIONAL RESEARCH FELLOW IN CHEMISTRY.

² Wöhler, *Ann.*, **51**, 1844 (145-63).

³ F. Mylius, *Ber.*, **18**, 1885 (467).

⁴ F. Kehrman, *Ibid.*, **23**, 1890 (906).

⁵ A. Hofmann, *Jahr.*, 1863 (415).

⁶ F. Fichter, *Ann.*, **361**, 1908 (397, 400).

⁷ F. Fichter, and A. Willmann, *Ber.*, **37**, 1904 (2388).

⁸ Th. Zincke, *Ibid.*, **14**, 1881 (94).

⁹ R. T. Plimpton, *J. Chem. Soc.*, **37**, 1880 (637).

THE GRATING SPACE OF MICA AND THE INTENSITIES OF THE SPECTRAL ORDERS

BY BERGEN DAVIS AND H. M. TERRILL

PHOENIX PHYSICAL LABORATORY, COLUMBIA UNIVERSITY

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In attempting to determine the reflectivity from its principal cleavage planes, it was found desirable to know the grating space and incidentally the relative intensities of the several spectral orders.

We would like to point out that perhaps the grating space of mica may not be constant. The thickness of a piece of mica may be altered by pressure to a small extent without apparently destroying its crystalline structure. In this case we should expect natural specimens even of the same chemical constitution to show differences due to the variable pressures to which they may have been subjected in their natural positions in the native rocks.

The specimen of mica here reported on was a clear sheet about one millimeter in thickness. It was selected for its smoothness of surface and freedom from flaws. Nevertheless it was not optically plane as shown by viewing a distant straight edge by reflection from the surface. Small local departures from a plane surface were evident.

The measurements were made by an ionization spectrometer, the standards of wave-lengths were the $K_{\alpha_1}(\lambda = .710)$ and the $K_{\beta_1}(\lambda = .633)$ emitted from a Coolidge tube having a molybdenum target. The slit of the ionization chamber was left open wide, the readings of angular position being made only on the crystal verniers.